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Preparation and Conformational Properties of Several 1,8-Diarylnaphthalenes

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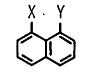
Six new 1,8-diarylnaphthalenes, each having closely held parallel aromatic rings, were synthesized by a Kharash-type Grignard cross-coupling of arylmagnesium iodide and 1,8-diiodonaphthalene in the presence of *N,N′*-bis(1-methyl-3-oxobutylidene)ethylenediaminatonickel(II) as a catalyst. Among them, 1,8-di(1-naphthyl)naphthalene was obtained as *cis* and *trans* rotamers, caused by the restricted rotation at the 1,8-position. Interconversion between the rotamers on heating above their melting points was confirmed by differential scanning calorimetry. The proton magnetic resonance spectral studies of the 1,8-diarylnaphthalenes indicated the presence of a face-to-face arrangement of aromatic rings in the peri-position. Two new 8,8′-diaryl-1,1′-binaphthyls, each having two sets of closely held parallel aromatic rings, were isolated as minor coupling products. *Trans-trans* conformations were proposed for them on the basis of their thermal behavior. Several nickel(II) complexes were found to be effective catalysts for preparative Grignard cross-coupling reaction involving closely crowded geometry.

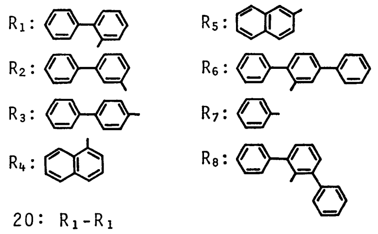
A number of compounds having closely held parallel aromatic rings, *e.g.* paracyclophanes,1) janusene,2) 1,8-diarylnaphthalenes,3) diarylanthracenes,4) have been synthesized and studied extensively in view of their specific geometry and their inherent strain due to steric overcrowding. Most of their unusual properties have been ascribed to the existence of such molecules in conformations in which the two benzene rings lie parallel to one another. Recently, Clough and Roberts5) have found that 1,8-di(*o*-tolyl)naphthalene could be resolved into *cis* and *trans* isomer pair due to a restricted rotation around the tolyl-naphthyl bonds. The two isomers were found to be stable in the crystalline state, but interconversible in solution having a half-life of about one day at room temperature.

The present study was undertaken to synthesize stable rotational isomer pairs of a series of closely related 1,8-diarylnaphthalenes having adjacent parallel π-systems, and to elucidate their structure-physical property correlations. Thus six new 1,8-diarylnaphthalenes (**1**—**6**), having biphenylyl, naphthyl, or terphenylyl groups in the peri-position, were synthesized. Their infrared (IR), ultraviolet (UV), and proton magnetic resonance (^{1}H-NMR) spectra were measured, and the relationship is discussed between the structures and physical properties of the diarylnaphthalenes, especially the characteristics due to the presence of adjacent face-to-face arrangement of two benzene rings. In addition, the characterization and interconversion of the stable *cis* and *trans* rotational isomers of 1,8-di(1-naphthyl)naphthalene (**4**) are also described.

For the synthesis of 1,8-diarylnaphthalenes, the Kharash-type Grignard cross-coupling reaction of the Grignard reagent derived from an appropriate aryl iodide and 1,8-diiodonaphthalene in the presence of nickel(II) complex as a catalyst was employed. Though the similar cross-coupling reaction has already been used for the synthesis of 1,8-di(*o*-tolyl)naphthalene,5) we introduced the diarylnaphthalenes under modified reaction conditions.

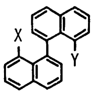


1: X=Y=R$_1$
2: X=Y=R$_2$
3: X=Y=R$_3$
4: X=Y=R$_4$
5: X=Y=R$_5$
6: X=Y=R$_6$
7: X=Y=R$_7$
8: X=Y=I
9: X=H, Y=R$_1$
10: X=H, Y=R$_2$
11: X=H, Y=R$_3$
12: X=H, Y=R$_4$
13: X=H, Y=R$_5$
14: X=H, Y=R$_7$
15: X=I, Y=R$_8$



20: R$_1$-R$_1$
21: R$_2$-R$_2$
22: R$_3$-R$_3$
23: R$_5$-R$_5$
24: R$_6$-R$_6$
25: R$_8$-R$_8$

26: R$_1$I
27: R$_2$I
28: R$_3$I
29: R$_4$I
30: R$_5$I
31: R$_6$I
32: R$_7$I
33: R$_8$I



16: X=Y=R$_1$
17: X=Y=R$_4$
18: X=Y=R$_7$
19: X=I, Y=R$_8$

Preliminary experiments using phenylmagnesium iodide and each of two nickel(II) complexes, bis(acetylacetonato)nickel(II) [Ni(acac)$_2$] and *N,N′*-bis(1-methyl-3-oxobutylidene)ethylenediaminatonickel(II) [Ni(acaen)],6,7) to provide 1,8-diphenylnaphthalene (**7**) indicated that the relative activities of the two complexes were essentially the same (the yields of **7** are 67 and 66%, respectively). Furthermore, alternate preliminary experiments using 1-naphthylmagnesium iodide and each of the following nickel(II) complexes to provide 1,8-di(1-naphthyl)naphthalene showed that all the complexes except potassium tris(L-prolinato)niccolate(II) trihydrate [K[Ni(L-pro)$_3$]·

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$3H_2O$][8] effectively catalyzed the coupling reaction involving considerably crowded geometry: Ni(acac)$_2$, Ni(acaen), bis(4-imino-2-pentanonato)nickel(II) [Ni(acNH)$_2$],[8] bis(η-cyclopentadienyl)nickel(II) [Ni(C_5H_5)$_2$],[8] bis(salicylaldehydato)nickel(II) dihydrate [Ni(sal)$_2$·$2H_2O$],[8] bis(trifluoroacetylacetonato)nickel(II) [Ni(tfa)$_2$],[8] and K[Ni(L-pro)$_3$]·$3H_2O$ (Table 1). On the basis of the foregoing results, Ni(acaen) was used as a catalyst in the preparative experiments.

Among the iodo compounds used, iodobiphenyls[9] (2- (**26**), 3- (**27**), and 4-iodobiphenyl (**28**)) and 2′-iodo-*p*-terphenyl (**31**)[10] were prepared by the methods previously reported. 2′-Iodo-*m*-terphenyl (**33**) was derived by the Ullmann coupling of 1,3-dibromo-2-nitrobenzene and iodobenzene,[11] followed by reduction and then conversion into the iodo compound by the usual method. Although, 1-iodo- (**29**) and 1,8-diiodonaphthalene (**8**)[4] were prepared from corresponding amino compounds, 2-iodonaphthalene (**30**) and iodobenzene (**32**) were commercially available.

The coupling reaction was proceeded by adding a solution of diiodo compound (**8**) and nickel(II) complex (0.1—0.3 mol%) in benzene as a single batch to a refluxing solution of each arylmagnesium iodide (4 fold to 8 fold excess) in an ether–benzene mixture. The reaction products were subjected to column chromatography on alumina. The 1,8-diarylnaphthalenes (**1**—**7**)[12] and by-products thus obtained are given in Table 2.

TABLE 1. CATALYTIC ACTIVITY OF VARIOUS NICKEL COMPLEXES FOR THE CROSS-COUPLING OF 1-$C_{10}H_7MgI$ WITH $C_{10}H_6I_2$(1,8-) (**8**)[a)]

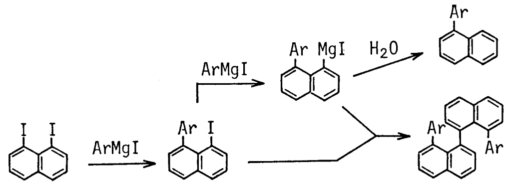
Catalyst	Conversion of **8**	Products (Yield/%)[b)]		
	%	**4**	**17**	**29**
None	91.3	3.2	0	70.2
Ni(acac)$_2$	100	40.8	17.6	1.8
Ni(acaen)	100	42.2	16.2	3.0
Ni(acNH)$_2$	100	43.5	19.2	1.8
Ni(C_5H_5)$_2$	100	38.6	18.0	4.2
Ni(sal)$_2$·$2H_2O$	100	37.4	15.8	2.8
Ni(tfa)$_2$	100	37.4	17.6	3.2
K[Ni(L-pro)$_3$]·$3H_2O$	100	12.3	4.2	4.9

a) Determined by quantitative GLPC, using triphenylamine as an internal standard calibrated against the pure samples. b) Based on the **8** used.

TABLE 2. SYNTHESES OF 1,8-DIARYLNAPHTHALENES BY THE GRIGNARD CROSS-COUPLING OF ArMgI WITH $C_{10}H_6I_2$(1,8-) (**8**)

ArI in ArMgI	Diarylnaphthalene (Yield/%)	Other products
32	**7** (58)	**14**, **18**
26	**1** (27)	**9**, **16**, **20**
27	**2** (41)	**10**, **21**
28	**3** (42)	**11**, **22**
29	**4** (37)	**12**, **17**
30	**5** (31)	**13**, **23**
33	—	**15**, **19**, **25**
31	**6** (11)	**24**

The hitherto-unknown 1,8-diarylnaphthalenes (**1a**, **1b**, **2**, **3**, **4a**, **4b**, **5**, and **6**) thus prepared and 8,8′-diaryl-1,1′-binaphthyl (**16** and **17**) thus isolated as minor products, gave satisfactory analytical results and spectral data (IR, UV, and MS) consistent with the indicated structures. In the coupling reaction, rather low yields of diarylnaphthalenes (**1**—**5**) (27—42%) as compared with that of **7** (58%) may due to enhanced overcrowded conformations of the formers. Furthermore, a very low yield of **6** (11%) and unsuccessful result in the attempted coupling of **8** and Grignard reagent derived from **33**, may also be attributable to the steric crowd during the course of the reactions. The table also shows the formation of 1-arylnaphthalenes (**9**—**14**)[13] and 8,8′-diaryl-1,1′-binaphthyls (**16**—**18**) as common and uncommon by-products, respectively. These by-products formations may reasonably be ascribed to have proceeded *via* the process of Grignard exchange[14] between the Grignard reagent and the iodo compound as follows. In most of the coupling reactions, homo-coupling products (**20**—**25**) of the Grignard reagents were also isolated.

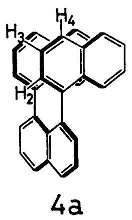


Among the diarylnaphthalenes, **1** was obtained in two forms, **1a** (plates, mp 144.8—145.7 °C) and **1b** (needles, mp 150.3—151.3 °C), from cyclohexane. Repeated crystallizations of **1a** from ethanol yielded **1b**. Both **1a** and **1b** gave slightly different IR spectra, but practically identical ^{1}H-NMR, UV, and mass spectra. The DSC curve for melting of **1a** showed an endothermic peak at 144 °C. After two weeks' annealing period, however, the second run of the melt showed two peaks at 144 °C and 149 °C. While, the DSC curve of **1b** showed a peak originally at 150 °C, after two weeks the second run of the melt showed a new small peak at 144 °C together with the original one at 149 °C. The thermoanalytical analyses suggest the formation of an equilibrium mixture of **1a** and **1b** at or above 150 °C. Though lacking a conclusive proof, it seems very likely that **1a** and **1b** are a rotational isomer pair.

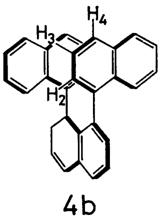
On the other hand, **4** was obtained as more soluble needles **4a** (mp 155.4—156.8 °C) and less soluble plates **4b** (mp 173.3—174.2 °C) in a benzene–ethanol mixture. Both **4a** and **4b** revealed similar UV, slightly different IR, and different ^{1}H-NMR spectra which were found to be compatible with *cis* and *trans* conformations, respectively. The DSC curve of **4a** showed endothermic peaks at 158 °C and 173 °C, having approximately the intensities of 2:1. After cooling, the second run of the melt also showed two peaks at practically the same temperatures but having reverse intensities of 1:5. Further run of the melt did not exhibit any appreciable change compared with that of the second. However, **4b** displayed at first only one peak at 174 °C. The second run of the melt showed practically the same DSC curve as that of the second run of **4a**, having two peaks at 157 °C and 173 °C with approximate intensities of 1:5. In addition, ^{1}H-NMR spectra ($CDCl_3$) of both melts of each second run of **4a** and **4b** are superimposable, and are compatible to that of a mixture of **4a** and **4b**. On the basis of the foregoing results, it was clarified that **4a** (*cis*) and **4b** (*trans*) were interconversible by heating, and that either of **4a** (*cis*) and **4b** (*trans*) formed same equilibrium mixture of a ratio of approximately 1:4 at or above 176 °C.[15] Both rotamers **4a** and **4b** are quite stable in a solution ($CDCl_3$) at room temperature over two weeks. The stability seems to be remarkable as compared with the half-life of only about one day in solution with respect to interconversion between *cis* and *trans* of 1,8-di(*o*-tolyl)naphthalene at room temperature.[5] Though the *cis* rotamer **4a** would be achiral, the *trans* rotamer **4b** would be a racemic mixture. Identification of the antipodes by resolution was not attempted.

Another crowded diarylnaphthalene, **6** was obtained as colorless needles mp 225.6—227.6 °C, presumably having a *trans* conformation on the basis of its heat stable character.[16] Analogously, both heat stable 8,8′-diaryl-1,1′-binaphthyls, **16** and **17**, may possibly be considered to have *trans-trans* conformations.[16] Although, each of these compounds, **6**, **16**, **17**, and **18**, would be a racemic mixture, their resolutions were not attempted. Each of the other diarylnaphthalenes (**2**, **3**, and **5**) proved to be single substances suggesting a sufficiently low energy barrier to rotation of two aryl rings around the bonds at the peri-position.[4]

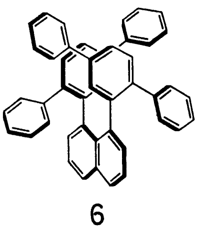
The IR spectra of the 1,8-diarylnaphthalenes and related compounds were measured by the KBr-disk method and their characteristic bands in the 680—915 cm^{-1} region were tentatively assigned. These bands are consistent with the kinds of aryl groups and naphthalene ring(s) comprising each of the compounds. All of the compounds show very similar spectra to those of polyphenyls.[9–11] In addition, the characteristic C–C out-of-plane bending vibration bands of substituted naphthalene were observed commonly in the 800—850 cm^{-1} region. However, no significant spectral differences between 1-aryl- and corresponding 1,8-diarylnaphthalenes (presumably due, if any, to the face-to-face arrangement of two benzene or naphthalene rings in the peri-position) were noticed.



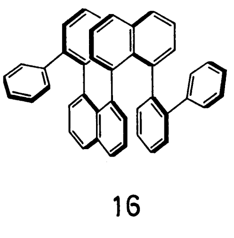
4a



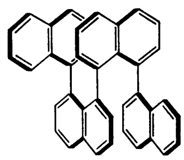
4b



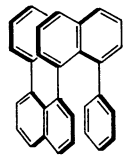
6



16



17



18

The slightly different spectra of **4a** and **4b** in the regions 770—780 cm^{-1} and 820—840 cm^{-1}, assignable to C–H out-of-plane bending on the 1-naphthyl ring and to C–C out-of-plane bending of the naphthalene ring, may be ascribed to their *cis* and *trans* conformation, respectively.

The UV spectra of the 1,8-diarylnaphthalenes and related compounds were measured in cyclohexane solution.

The absorption curves of **4** and **17** were related closely to that of **12**, which corresponds to structural unit of **4** and **17**. Thus, a blue shift and an increase in intensity of the band at 223 nm of **12** with an increase of 1-naphthyl unit were observed.

The spectra of the *cis* rotamer **4a** and the *trans* rotamer **4b** were found to be practically identical. This suggests the lack of significant transannular π-electronic interaction between parallel peri-naphthyl rings of **4a** and **4b**, presumably due to the remote distance of the parallel rings beyond the limit of interaction.[17] Both spectra of 8,8′-diaryl-1,1′-binaphthyls, **18** and **16**, showed similarly a significant red shift (near 316 nm) as compared with that of simpler analog **12**. However, it is difficult to ascertain whether the shifts are due to an increase of aromatic rings[18] or to the transannular π-electronic interaction of parallel aromatic rings. Among the spectra of 1,8-di(biphenylyl)-naphthalenes, that of **3** revealed an increase in intensity of the E-band and a red shift of the longest wavelength absorption band as compared with that of **11**. The spectral differences of **1** with **9**, and of **2** with **10** are essentially similar to that of **7** with **14**.

The foregoing UV spectral results indicated that no significant influence originated from the face-to-face arrangement of the aromatic rings in the peri-positions.

The ^{1}H-NMR spectra of the diarylnaphthalenes and related compounds were measured at 80 MHz in $CDCl_3$ solution.

In the spectrum of the simplest 1,8-diarylnaphthalene **7**, a sharp singlet of phenyl protons appears at higher field by approximately 0.5 ppm compared with that of the monoaryl analog **14**, owing to the anisotropic effect of the faced benzene rings. This high field shift may be comparable to those observed for the faced aromatic protons of [2.2]paracyclophane (δ 6.37)[19] and of janusene (δ 6.60)[2a] as compared with those of *p*-xylene (δ 7.05)[20] and of *o*-xylene (δ 7.10),[2a] respectively. In the spectra of **1**, **2**, and **5**, the aromatic proton signals were also observed at rather high field region as compared with those of corresponding monoaryl analogs **9**, **10**, and **13**, suggesting the presence of a face-to-face arrangement of benzene or 2-naphthyl rings in the peri-position. In the case of **3**, a sharp singlet, which can be assigned to the protons of both phenyl rings, is observed at lower field than that of **7** but similar to that of **14**, indicating that the faced phenyl rings are situated further apart from each other than in **7**.

In the spectrum of isomer **4b**, the chemical shift of naphthyl-C_4 protons (δ 7.03) is nearly comparable to that of the phenyl protons of **7**, whereas the signals of naphthyl-C_2,C_3 protons are shifted appreciably toward higher field presumably owing to the ring current effects caused by the partially parallel naphthyl rings. Analogous but more prominent upfield shifts over 1 ppm have been observed in the spectrum of *anti*-[2.2](1,4)anthracenophane, in which C_2, C_3-protons were located nearly above the opposed anthracene ring.[21] Spectrum of isomer **4a**, however, shows quite different signal pattern of naphthyl-C_2,C_3,C_4-protons (δ 7.00—6.65), but similar signals for other protons in the spectrum of **4b**. Although an assignment of the former pattern is difficult, lack of the characteristic signals of **4b** in the high filed region (δ 6.50—6.14) reflects undoubtedly the absence of protons located nearly above the opposite naphthalene ring.

Thus the foregoing spectral aspects on **4a** and **4b** are obviously compatible with the proposed conformations as *cis* and *trans* rotamers, respectively.

Experimental

Instruments. Low melting points were determined with a Mettler FP-51 or FP-52 apparatus; for those above 300 °C, a Shimadzu DSC-30M differential scanning calorimeter was employed. The calorimeter was also used for thermoanalytical purpose. The UV spectra were measured on a Shimadzu MPS-50L spectrophotometer, IR spectra on a Leitz III-G spectrophotometer, and ^{1}H-NMR spectra on a Varian CFT-20 spectrometer at 80 MHz, using TMS as an internal standard. The molecular weights were determined with a Hitachi RMU-6E mass spectrometer. Quantitative GLPC was performed on a Shimadzu GC-5APTF gas chromatograph using a 1 m×3 mm ϕ glass column 3% Silicone OV-17 on Chromosorb W AW-DMCS.

Materials. 2- (**26**), 3- (**27**), and 4-Iodobiphenyl (**28**),[9] 2′-iodo-*p*-terphenyl (**31**),[10] *N*,*N*′-bis(1-methyl-3-oxobutylidene)ethylenediaminatonickel(II), bis(4-imino-2-pentanonato)nickel(II), bis(salicylaldehydato)nickel(II) dihydrate, bis(trifluoroacetonato)nickel(II), and potassium tris(L-prolinato)niccolate(II) trihydrate[7] were prepared as reported previously. 2′-Iodo-*m*-terphenyl (**33**) was prepared by the Ullmann cross-coupling of 1,3-dibromo-2-nitrobenzene[11] and iodobenzene, followed by reduction and iodosubstitution of the corresponding diazonium compound. Colorless prisms, mp 114.4 °C (Found: C, 60.99; H, 3.87%. Calcd for $C_{18}H_{13}I$: C, 60.69; H, 3.68%). 1-Iodonaphthalene (**29**) was prepared from 1-aminonaphthalene by the usual method. A colorless oil, bp 117—121 °C/2.66×10^2 Pa. 1,8-Diiodonaphthalene (**8**) was prepared by the method used by House *et al.*[4] Tan prisms, mp 110 °C (lit,[4] mp 108.5—110 °C) (Found: C, 31.88; H, 1.63%). 2-Iodonaphthalene (**30**), iodobenzene (**32**), bis(acetylacetonato)nickel(II), and bis(η-cyclopentadienyl)nickel(II) were commercially available.

General Procedure of Grignard Cross-coupling. Magnesium turnings were placed in a four-necked round-bottomed flask equipped with a reflux condenser. To the flask was added *ca.* 20% of an ethereal solution of aryl iodide (*c*: 0.8—1.0 mol dm^{-3}) under nitrogen atmosphere, and the mixture was stirred and (if necessary) heated to initiate the reaction. The remaining aryl iodide solution was added dropwise just rapidly enough to maintain a gentle reflux (*ca.* 45 min). After additional 0.5 h heating, the resulting solution was diluted with half its volume of benzene. To the refluxing Grignard reagent was added all at once a hot benzene solution of **8** (*c*: 0.3 mol dm^{-3}) and a catalyst Ni(acaen) (0.13 mol%, based on Grignard reagent), and the reflux then continued to complete the reaction. After cooling, the mixture was hydrolyzed with concentrated ammonium chloride solution. The resulting mixture was extracted with benzene. The organic layer was separated, washed with water, and then dried. The crude mixture, remaining after removal of the solvent, was subjected to chromatography on alumina with a mixture of cyclohexane and benzene as eluent to separate into each product.

Preparation of 1,8-Diphenylnaphthalene (7). The Grignard reagent prepared from the aryl iodide **32** (4.90 g, 24 mmol) was treated with **8** (2.28 g, 6 mmol) in the presence of Ni(acaen) (8.4 mg, 0.03 mmol) and the mixture was refluxed for additional 10 min, as described in the general procedure. The benzene extract of the product was chromatographed on alumina with a cyclohexane–benzene (9:1, v/v) mixture (C–B(9:1)) to separate into the following compounds.

7: Colorless needles from cyclohexane; mp 151.0 °C lit,[3a] mp 149.5—150.5 °C); yield, 0.98 g (58.0%). IR: 698 vs, 706 m ($\gamma_{\text{C-C}}$, B); 750 s, 758 s, 765 m ($\gamma_{\text{C-H}}$, M); 775 vs ($\gamma_{\text{C-H}}$, d); 829 s, 843 m ($\gamma_{\text{C-C}}$, N); 880 w.[22] UV: $\lambda_{\max}(\varepsilon)$ 198 (42400), 215 (39900), 237 (57700), 302 nm (12000) (lit,[3a] $\lambda_{\max}(\varepsilon)$ (95% ethanol) 235.5 (54500), 300 nm (11500)). ^{1}H-NMR δ: 6.89 (10H, s, C_6H_5); ν_2 7.36, ν_3 7.49, ν_4 7.90 (6H, $J_{2,3}$=7.0 Hz, $J_{3,4}$=8.5 Hz, $J_{2,4}$=1.4 Hz, $C_{10}H_6$). (Found: C, 94.38; H, 5.92%; mol wt, 280 (M^+)).

1-Phenylnaphthalene (**14**): A colorless oil (lit,[23] bp 147—154 °C/133—160 Pa); 0.18 g (14.8%). IR: 702 s ($\gamma_{\text{C-C}}$, B); 735 w; 758 s ($\gamma_{\text{C-H}}$, M); 775 s ($\gamma_{\text{C-H}}$, α); 800 s ($\gamma_{\text{C-H}}$, α; $\gamma_{\text{C-C}}$, N); 840 w ($\gamma_{\text{C-C}}$, N); 866 w, 909 w. UV: $\lambda_{\max}(\varepsilon)$ 227 (65200), 288 nm (10900). ^{1}H-NMR δ: 7.42 (5H, s, C_6H_5), 7.30—8.00 (7H, m, other protons).

8,8′-Diphenyl-1,1′-binaphthyl (**18**): Colorless prisms from cyclohexane; mp 208.9—210.7 °C (lit,[4] mp 210.5—212.0 °C); 0.15 g. IR: 696 vs, 709 m ($\gamma_{\text{C-C}}$, B); 750 m, 763 s ($\gamma_{\text{C-H}}$, M); 770 vs ($\gamma_{\text{C-H}}$, d); 821 s, 831 m ($\gamma_{\text{C-C}}$, N). UV: $\lambda_{\max}(\varepsilon)$ 195 (55200), 220 (52600), 240 (sh) (34800), 318 nm (12700) (lit,[4] $\lambda_{\max}(\varepsilon)$ (95% ethanol), 221 (58000), 248 (sh) (29000), 285 (11000), 315 nm (12000)). ^{1}H-NMR δ: 6.05—6.65 (10H, m, C_6H_5), 6.90—7.63 (12H, m, $C_{10}H_6$). (Found: C, 94.82; H, 5.71%; mol wt, 406 (M^+)).

Perylene: Yellow plates from benzene; mp 274.7—275.7 °C (lit,[24] mp 274—275 °C); 0.01 g.

Preparation of 1,8-Di(2-biphenylyl)naphthalene (1). The Grignard reagent prepared from the aryl iodide **26** (48.8 g, 160 mmol) was treated with **8** (7.6 g, 20 mmol) in the presence of Ni(acaen) (0.14 g, 0.5 mmol), and the mixture was refluxed for additional 2 h. The benzene extract of the product, after removal by distillation under reduced pressure of a large part of the biphenyl and naphthalene, was subjected to chromatography on alumina with a C–B (9:1) mixture and separated into the following compounds.

1a: Obtained by concentration and cooling of the mother liquor of **1b**; colorless plates from cyclohexane; mp 144.8—

145.7 °C; 0.31 g (3.4%). IR: 697 sh s, 701 s ($\gamma_{\text{C-C}}$, B); 720 m, 738 vs, 747 m, 758 s ($\gamma_{\text{C-H}}$, M, *o*); 772 s ($\gamma_{\text{C-H}}$, d); 829 s, 847 w ($\gamma_{\text{C-C}}$, N). Repeated crystallizations of **1a** from cyclohexane or ethanol gave **1b**.

1b: Colorless needles from cyclohexane; mp 150.3—151.3 °C; 2.12 g (23.3%). IR: 701 s, 706 sh s ($\gamma_{\text{C-C}}$, B); 720 m, 740 vs, 752 s ($\gamma_{\text{C-H}}$, M, *o*); 775 s ($\gamma_{\text{C-H}}$, d); 831 s, 846 w ($\gamma_{\text{C-C}}$, N). UV: $\lambda_{\max}(\varepsilon)$ 204 (72500), 218 (sh) (65100), 244 (sh) (42800), 294 nm (10100). ^{1}H-NMR δ: 7.60—7.65 (2H, q, C_4–, C_5–H of $C_{10}H_6$), 6.75—7.30 (22H, m, other protons). Found: C, 94.70; H, 5.32%; mol wt, 432 (M$^+$). Calcd for $C_{34}H_{24}$: C, 94.40; H, 5.60%; mol wt, 432.

1-(2-Biphenylyl)naphthalene (**9**): Colorless fine needles from ethanol; mp 113.2—114.4 °C; 1.32 g (22.4%). IR: 699 s ($\gamma_{\text{C-C}}$, B); 738 m, 745 s, 751 s ($\gamma_{\text{C-H}}$, M, *o*, α); 770 s ($\gamma_{\text{C-H}}$, *o*, α); 780 vs, 795 m ($\gamma_{\text{C-H}}$, α); 803 s ($\gamma_{\text{C-H}}$, α; $\gamma_{\text{C-C}}$, N); 866 w, 882 w. UV: $\lambda_{\max}(\varepsilon)$ 205 (59300), 225 (60200), 290 nm (9600). ^{1}H-NMR δ: 7.00 (5H, s, C_6H_5), 7.18—7.90 (11H, m, *o*-C_6H_4 and $C_{10}H_7$). Found: C, 94.35; H, 5.83%. Calcd for $C_{22}H_{16}$: C, 94.24; H, 5.76%.

trans, *trans*-8,8′-Di(2-biphenylyl)-1,1′-binaphthyl (**16**): Colorless plates from hexane; mp 270.8—272.1 °C; 0.46 g. IR: 705 s ($\gamma_{\text{C-C}}$, B); 737 s, 743 vs, 755 s ($\gamma_{\text{C-H}}$, M, *o*); 762 sh m, 772 vs ($\gamma_{\text{C-H}}$, d); 820 m, 830 m, 849 w ($\gamma_{\text{C-C}}$, N); 866 w. UV: $\lambda_{\max}(\varepsilon)$ 203 (81400), 224 (77200), 254 (sh) (33300), 316 nm (10400). ^{1}H-NMR δ: 6.25—7.65 (30H, m, all protons). Found: C, 94.30; H, 5.17%; mol wt, 558 (M$^+$). Calcd for $C_{44}H_{30}$: C, 94.58; H, 5.42%; mol wt, 558.

1,1′:2′,1″:2″,1‴-Quaterphenyl (**20**): Colorless cubes from ethanol; mp 118.7 °C (lit,[9] mp 118—119 °C); 1.86 g.

Preparation of 1,8-Di(3-biphenylyl)naphthalene (2). The Grignard reagent prepared from the aryl iodide **27** (16.8 g, 60 mmol) was treated with **8** (3.8 g, 10 mmol) in the presence of Ni(acaen) (20 mg, 0.07 mmol), and the mixture was refluxed for additional 2.5 h. The benzene extract, after removal by distillation of a large part of the biphenyl and naphthalene, was chromatographed on alumina with C–B(9:1), C–B(4:1), and finally with C–B(1:1).

2: Colorless needles from benzene–ethanol; mp 148.4—150.3 °C; 1.79 g (41.4%). IR: 697 s, 706 s ($\gamma_{\text{C-C}}$, B); 754 s, 756 s ($\gamma_{\text{C-H}}$, M); 778 s ($\gamma_{\text{C-H}}$, *m*, d); 799 m ($\gamma_{\text{C-H}}$, *m*, d; $\gamma_{\text{C-C}}$, N); 833 s, 849 w ($\gamma_{\text{C-C}}$, N); 892 m ($\gamma_{\text{C-H}}$, *m*). UV: $\lambda_{\max}(\varepsilon)$ 204 (70900), 231 (67100), 302 nm (15100). ^{1}H-NMR δ: 7.85—8.01 (2H, q, C_4–, C_5–H of $C_{10}H_6$), 6.90—7.63 (32H, m, other protons). Found: C, 94.11; H, 5.33%; mol wt, 432 (M$^+$). Calcd for $C_{34}H_{24}$: C, 94.40; H, 5.60%; mol wt, 432.

1-(3-Biphenylyl)naphthalene (**10**): A colorless oil; 1.02 g (36.7%). IR: 690 m, 698 s, 707 s ($\gamma_{\text{C-C}}$, B); 754 s ($\gamma_{\text{C-H}}$, M, α); 778 s, 792 s ($\gamma_{\text{C-H}}$, *m*, α); 799 s ($\gamma_{\text{C-H}}$, *m*, α; $\gamma_{\text{C-C}}$, N); 848 w ($\gamma_{\text{C-C}}$, N); 865 w; 897 m ($\gamma_{\text{C-H}}$, *m*). UV: $\lambda_{\max}(\varepsilon)$ 205 (49600), 225 (59200), 292 nm (sh) (11400). ^{1}H-NMR δ: 7.30—8.08 (16H, m, all protons). Found: C, 94.02; H, 5.78%. Calcd for $C_{22}H_{16}$: C, 94.24; H, 5.76%.

1,1′:3′,1″:3″,1‴-Quaterphenyl (**21**): Colorless leaves from ethanol; mp 87.1 °C (lit,[9] mp 86—87 °C); 1.46 g.

Preparation of 1,8-Di(4-biphenylyl)naphthalene (3). The aryl iodide **28** (16.8 g, 60 mmol), **8** (3.8 g, 10 mmol), and Ni(acaen) (56 mg, 0.2 mmol) were worked up as described in the general procedure, and the mixture was refluxed for additional 3 h. The benzene extract was concentrated to separate a solid (1,1′:4′,1″:4″,1‴-quaterphenyl, **22**, colorless leaves). After filtration of the solid, the mother liquor was distilled to remove a large part of the biphenyl and naphthalene. The resulting residue was chromatographed on alumina with C–B(3:1), C–B(2:1), and finally with C–B(1:2).

3: Colorless needles from benzene–ethanol; mp 202.4—203.8 °C; 1.83 g (42.4%). IR: 699 s, 704 m ($\gamma_{\text{C-C}}$, B); 733 s, 762 s, 766 s ($\gamma_{\text{C-H}}$, M); 781 s ($\gamma_{\text{C-H}}$, d); 829 s, 842 s ($\gamma_{\text{C-H}}$, *p*; $\gamma_{\text{C-C}}$, N); 885 w. UV: $\lambda_{\max}(\varepsilon)$ 200 (73300), 214 (sh) (59200), 241 (43700), 254 (35000), 304 nm (23300). ^{1}H-NMR δ: 7.11 (8H, d, J=1.5 Hz, *p*-C_6H_4), 7.27 (10H, s, C_6H_5), 7.35—7.73 (4H, m, C_2–, C_3–, C_6–, C_7–H of $C_{10}H_6$), 7.90—8.10 (2H, q, C_4–, C_5–H of $C_{10}H_6$). Found: C, 94.34; H, 5.89%; mol wt, 432 (M$^+$). Calcd for $C_{34}H_{24}$: C, 94.40; H, 5.60%; mol wt, 432.

1-(4-Biphenylyl)naphthalene (**11**): Colorless needles from benzene–ethanol; mp 149.3—150.7 °C (lit,[25] mp 147—148 °C); 0.59 g (19.2%). IR: 697 s ($\gamma_{\text{C-C}}$, B); 729 m; 739 w, 751 m, 765 vs ($\gamma_{\text{C-H}}$, M, α); 781 vs, 792 m ($\gamma_{\text{C-C}}$, α); 800 s ($\gamma_{\text{C-H}}$, α; $\gamma_{\text{C-C}}$, N); 837 m, 848 w ($\gamma_{\text{C-H}}$, *p*; $\gamma_{\text{C-H}}$, N); 873 w. UV: $\lambda_{\max}(\varepsilon)$ 209 (42200), 228 (45400), 262 (16400), 294 nm (19000). ^{1}H-NMR δ: 7.30—8.10 (16H, m, all protons). (Found: C, 94.41; H, 5.62%).

Preparation of 1,8-Di(1-naphthyl)naphthalene (4). The aryl iodide **29** (20.3 g, 80 mmol), **8** (3.8 g, 10 mmol), and Ni(acaen) (70 mg, 0.25 mmol) were worked up as described for the preparation of **3**. The benzene extract, after removal by distillation under reduced pressure of a large part of the naphthalene, was chromatographed on alumina with C–B(9:1), C–B(4:1), and finally with C–B(1:1). Crystallization of the eluate with C–B(9:1) from benzene–ethanol afforded **4b**. After filtration of **4b**, the mother liquor was concentrated to afford **4a**.

cis-1,8-Di(1-naphthyl)naphthalene (**4a**): Colorless needles from benzene–ethanol; mp 155.4—156.8 °C; 0.46 g (12.2%). IR: 713 w, 724 w, 770 vs, 772 vs, 781 sh s ($\gamma_{\text{C-H}}$, α); 792 s, 796 s ($\gamma_{\text{C-H}}$, α, d); 824 w, 837 m ($\gamma_{\text{C-C}}$, N); 860 w. UV: $\lambda_{\max}(\varepsilon)$ 216 (115400), 294 nm (16700). ^{1}H-NMR δ: 6.65—7.00 (6H, m, C_2–, C_3–, C_4–H of $C_{10}H_7$), 7.10—7.64 (12H, m, C_2–, C_3–, C_6–, C_7–H of $C_{10}H_6$; C_5–, C_6–, C_7–, C_8–H of $C_{10}H_7$), 7.94—8.13 (2H, q, C_4–, C_5–H of $C_{10}H_6$). Found: C, 94.90; H, 5.58%; mol wt, 380 (M$^+$). Calcd for $C_{30}H_{20}$: C, 94.70; H, 5.30%; mol wt, 380.

trans-1,8-Di(1-naphthyl)naphthalene (**4b**): Colorless plates from benzene–ethanol; mp 173.3—174.2 °C; 0.93 g (24.4%). IR: 714 w, 729 w; 773 vs ($\gamma_{\text{C-H}}$, α); 792 s, 797 s ($\gamma_{\text{C-H}}$, α, d); 823 m, 837 w ($\gamma_{\text{C-C}}$, N); 861 w. UV: $\lambda_{\max}(\varepsilon)$ 216 (119700), 294 nm (15900). ^{1}H-NMR δ: ν_2 6.27, ν_3 6.43, ν_4 7.03 (6H, $J_{2,3}$=7.0 Hz, $J_{3,4}$=8.5 Hz, $J_{2,4}$=1.4 Hz, $C_{10}H_7$), 7.10—7.64 (12H, m, C_2–, C_3–, C_6–, C_7–H of $C_{10}H_6$; C_5–, C_6–, C_7–, C_8–H of $C_{10}H_7$), 7.94—8.13 (2H, q, C_4–, C_5–H of $C_{10}H_6$). Found: C, 94.76; H, 5.55%; mol wt, 380 (M$^+$). Calcd for $C_{30}H_{20}$: C, 94.70; H, 5.30%; mol wt, 380.

1,1′-Binaphthyl (**12**): Colorless plates from benzene–ethanol; mp 158.8 °C (lit,[26] mp 147.5 °C); 2.35 g. IR: 740 m, 743 w, 770 vs, 779 vs, 783 vs ($\gamma_{\text{C-H}}$, α); 805 vs ($\gamma_{\text{C-H}}$, α; $\gamma_{\text{C-C}}$, N); 869 w. UV: $\lambda_{\max}(\varepsilon)$ 223 (75200), 284 (13400), 295 nm (13300) (lit,[27] $\lambda_{\max}(\varepsilon)$ (95% ethanol) 221 (95500), 283 (13200), 294 nm (12900)). ^{1}H-NMR δ: 7.17—8.05 (14H, m, all protons). (Found: C, 94.16; H, 5.73%).

trans,*trans*-8,8′-Di(1-naphthyl)-1,1′-binaphthyl (**17**): Colorless plates from benzene; mp 287.5—288.0 °C; 0.41 g. IR: 730 m; 770 vs ($\gamma_{\text{C-H}}$, α); 791 s, 796 m, 802 m ($\gamma_{\text{C-H}}$, α, d); 826 m, 834 m ($\gamma_{\text{C-C}}$, N); 865 w. UV: $\lambda_{\max}(\varepsilon)$ 212 (146400), 278 (16000), 306 nm (15100). ^{1}H-NMR δ: 6.48—7.69 (26H, m, all protons). Found: C, 95.08; H, 5.30%; mol wt, 506 (M$^+$). Calcd for $C_{40}H_{26}$: C, 94.82; H, 5.18%; mol wt, 506.

Preparation of 1,8-Di(2-naphthyl)naphthalene (5). The aryl iodide **30** (15.24 g, 60 mmol), **8** (3.8 g, 10 mmol), and

Ni(acaen) (56 mg, 0.2 mmol) were worked up as described for the preparation of **2**. The benzene extract, after removal by distillation under reduced pressure of a large part of the naphthalene, was subjected to crystallization from C–B-(9:1). After filtration of a solid (**23**), the solvent of the filtrate was distilled off. The residue was chromatographed on alumina progressively with C–B(9:1), C–B(5:1), C–B-(2:1), and finally with C–B(1:1) to give following compounds.

5: Colorless needles from benzene–ethanol; mp 142.4—144.7 °C; 1.16 g (30.5%). IR: 714 w; 738 s, 754 w (γ_{C-H}, β); 766 m, 775 s (γ_{C-H}, β, d); 804 m (γ_{C-H}, d); 814 s, 833 m, 854 m (γ_{C-H}, β; γ_{C-C}, N); 893 m (γ_{C-H}, β). UV: $\lambda_{max}(\varepsilon)$ 220 (sh) (98300), 227 (101200), 282 nm (19500). ^{1}H-NMR δ: 7.90—8.07 (2H, q, C_4–, C_5–H of $C_{10}H_6$), 6.90—7.88 (18H, m, other protons). Found: C, 94.96; H, 5.26%; mol wt, 380 (M$^+$). Calcd for $C_{30}H_{20}$: C, 94.70; H, 5.30%; mol wt, 380.

1,2′-Binaphthyl (**13**): Colorless needles from ethanol; mp 77.4 °C (lit,[26] mp 78 °C); 0.88 g (34.6%). IR: 737 m, 746 s, 777 s (γ_{C-H}, α, β); 794 m (γ_{C-H}, α); 801 s (γ_{C-H}, α; γ_{C-H}, N); 826 m, 833 m (γ_{C-H}, β; γ_{C-C}, N); 860 m, 866 w; 895 w (γ_{C-H}, β). UV: $\lambda_{max}(\varepsilon)$ 220 (72300), 227 (70300), 283 nm (17000) (lit,[28] $\lambda_{max}(\varepsilon)$ 219 (63100), 226 (61000), 272 (sh) (13500), 282 nm (15900)). ^{1}H-NMR δ: 7.32—7.70 (7H, m, 2-$C_{10}H_7$), 7.72—8.07 (7H, m, 1-$C_{10}H_7$). (Found: C, 94.72; H, 5.59%).

2,2′-Binaphthyl (**23**): Colorless plates from C–B(9:1); mp 186.6 °C (lit,[26] mp 187.0 °C); 0.74 g. IR: 738 s, 749 m (γ_{C-H}, β); 812 vs (γ_{C-C}, β; γ_{C-C}, N); 854 vs (γ_{C-C}, N); 883 s (γ_{C-H}, β). UV: $\lambda_{max}(\varepsilon)$ 205 (sh) (33300), 213 (44100), 248 (sh) (66700), 255 (97500), 272 (sh) (25700), 306 nm (18100) (lit,[27] $\lambda_{max}(\varepsilon)$ 212 (39800), 248 (sh) (63100), 254 (97700), 271 (sh) (27500), 280 (sh) (17000), 305 nm (19500)). ^{1}H-NMR δ: 7.22—8.22 (14H, m, all protons). (Found: C, 94.76; H, 5.57%).

*Reaction of **8** and Magnesium Compound of **33**.* Magnesium turnings (0.83 g, 34 mmol) were placed in a flask as described in the general procedure. To the flask was added a solution of **33** (12.1 g, 34 mmol) in a ether–benzene mixture (80 ml; 3:1, v/v) all at once, and the reaction mixture was refluxed for 5 h. The hot Grignard reagent thus prepared was treated with **8** (3.04 g, 8 mmol) in the presence of Ni(acaen) (22 mg, 0.08 mmol) and the mixture was refluxed for additional 3 h. The benzene extract of the product, after removal of the solvent, was subjected to crystallization from benzene to give 2,2′,6,6′-tetraphenylbiphenyl (**25**). After filtration of **25**, followed by removal of solvent from the filtrate, the residue was chromatographed on alumina with C–B(3:1).

1-Iodo-8-(*m*-terphenyl-2′-yl)naphthalene (**15**): Pale yellow needles from benzene–ethanol; mp 186.5—187.5 °C; 2.04 g. IR: 701 s (γ_{C-C}, B); 739 w; 753 s, 758 s (γ_{C-H}, M); 763 s, 767 s (γ_{C-H}, d); 804 m (γ_{C-H}, *as*); 818 w, 825 w (γ_{C-C}, N); 862 w. Found: C, 69.92; H, 4.20%; mol wt, 482 (M$^+$). Calcd for $C_{28}H_{19}I$: C, 69.70; H, 3.97%; mol wt, 482.

8-Iodo-8′-(*m*-terphenyl-2′-yl)-1,1′-binaphthyl (**19**): Colorless needles from benzene-ethanol; mp 263.6—266.2 °C; 0.05 g. IR: 699 s (γ_{C-C}, B); 747 m, 758 s (γ_{C-H}, M); 764 s (γ_{C-H}, d); 773 m (γ_{C-H}, d, *as*); 803 w (γ_{C-H}, *as*); 817 m, 827 w, 837 w (γ_{C-C}, N). Found: mol wt, 608 (M$^+$). Calcd for $C_{38}H_{25}I$: mol wt, 608.

25: Colorless cubes from benzene; mp 390 °C (lit,[29] mp 396 °C); 0.13 g.

*Preparation of 1,8-Di(*p*-terphenyl-2′-yl)naphthalene (**6**).* The Grignard reagent prepared from the aryl iodide **31** (4.98 g, 14 mmol) was treated with **8** (1.24 g, 3.25 mmol) in the presence of Ni(acaen) (9.1 mg, 0.033 mmol) as described for the preceding reaction. The benzene extract of the product, was crystallized to give *p*-terphenyl and 2,2′,5,5′-tetraphenylbiphenyl (**24**). After filtration of the solid, followed by removal of solvent from the filtrate, the residue was chromatographed on alumina with C–B(3:1).

trans-1,8-Di(*p*-terphenyl-2′-yl)naphthalene (**6**): Colorless needles from benzene–ethanol; mp 225.6—227.6 °C; 0.21 g (11.1%). IR: 700 s, 704 s (γ_{C-C}, B); 727 w, 740 m, 744 m, 757 s (γ_{C-H}, M); 779 s (γ_{C-H}, d); 826 w (γ_{C-C}, N); 835 m (γ_{C-C}, N; γ_{C-H}, *as*); 894 m (γ_{C-H}, *as*). UV: $\lambda_{max}(\varepsilon)$ 212 (84400), 225 (sh) (66400), 282 nm (50700). ^{1}H-NMR δ: 7.68—7.82 (2H, q, C_4–, C_5–H of $C_{10}H_6$), 6.63—7.55 (30H, m, other protons). Found: C, 94.74; H, 5.81%; mol wt, 584 (M$^+$). Calcd for $C_{48}H_{32}$: C, 94.48; H, 5.52%; mol wt, 584.

24: Colorless needles from ethanol; mp 194—195 °C (lit,[10] mp 194—195 °C); 0.11 g.

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13) These by-products were identified by mixed-melting-point determination (except **10**), elemental analyses, and comparison of the IR and UV spectra with those of samples prepared alternatively by the analogous Ni(acaen)-catalyzed Kharash-type Grignard cross-coupling of an appropriate Grignard reagent and 1-iodonaphthalene.

14) Clough *et al.* reported that the unfavorable formation of 1-phenylnaphthalene in the attempted coupling of ex-

cess of phenylmagnesium iodide and 1,8-diiodonaphthalene might have proceeded by the Grignard exchange between the both reactants (Ref. 3b).

15) The first scanning of the DSC determination of the melt, which consisted of the equilibrium mixture of **4a** and **4b**, was stopped at 169 °C (just before the second peak). After cooling, the next run of the melt showed only one peak at 174 °C, indicating that the melt used in the present scanning consisted of pure **4b**. The result was compatible with the ^{1}H-NMR spectrum of the melt used. The above experiment provides a novel procedure for obtaining the more stable rotamer in a pure state from an equilibrium mixture of the two rotamers. *Cf.* E. Ibuki, S. Ozasa, Y. Fujioka, and H. Mizutani, *Chem. Pharm. Bull.*, **29**, 2103 (1981).

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